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**UNDERPOTENTIAL DEPOSITION OF Cu ON Au(111): IMPLICATIONS OF THE HB
MODEL**

by

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UNDERPOTENTIAL DEPOSITION OF Cu ON Au(111): IMPLICATIONS OF THE HB MODEL

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April 30, 1994

Abstract

In recent papers [1, 2] a model for the underpotential deposition of Cu on Au(111) in the presence of bisulfate ions was proposed. In this model it was assumed that the bisulfate ions formed a $\sqrt{3} \times \sqrt{3}$ template. This template leaves a honeycomb lattice of free sites for the adsorption of copper. The clear implication is that the first peak has 2/3 of a monolayer of Cu. The second peak corresponds to the replacement of the bisulfate by copper in the adlayer. We showed also that the broad foot of the first peak is due to a second order hard hexagon like transition, which is seen experimentally by Itaya[3] and Kolb [4]. The interpretation, based on the STM and LEED observations, that the first peak corresponds to only 1/3 of a monolayer, is consistent with our model if it is the bisulfate ion that is actually seen in those experiments. In the present work we discuss further refinements of this theory: we show that from the dimensions of the bisulfate ion, an oxygen protrudes 1.84Å above the plane of copper adsorption, and the hydrogen of the bisulfate protrudes 2.13Å. Assuming the same geometry on a clean Au(111) surface the bisulfate layer should

stand about 4.1\AA above the surface. However, the STM cannot measure absolute heights, and therefore, both cases appear as a $\sqrt{3} \times \sqrt{3}$ overlayer. The dependence of the peak position with concentration is also discussed using a recently developed theory of kinetic effects.

1 Theory

The underpotential deposition (UPD) [5, 6] of metals frequently involves phase transitions that are observed in the voltammograms as sharp spikes [7, 8]. In earlier work [9, 10] we introduced a sticky adsorption site model to study phase transitions that occur when the adsorbate is commensurate with the substrate. This situation is known to occur, for example in the UPD of copper on gold (111) in the presence of bisulfate ions. As has been shown in earlier work [1, 2, 11] the particular structure of this voltammogram is due to a sequence of first and second order transitions taking place on the surface. To obtain sharp spikes in a voltammogram the substrate surface must be a perfect single crystal with large domain size. Slow scanning rates are also required. This immediately suggests that thermodynamic equilibrium and reversibility are necessary for the occurrence of these spikes, which are associated with first order phase transitions in the adsorbate layer [9, 10].

We should mention in this context the early work of Bewick and Thomas [12] who studied the case of UPD of Pb on Ag (111), and the work of Buess-Hermann[13] on the adsorption of alcohols on mercury. In both cases the mean field Frumkin's isotherm [14] was used to interpret the observations. We observe here that in both cases the adsorbed layer is incommensurate with the substrate, and in our theory the adsorbate must be commensurate. For the commensurate case Frumkin's isotherm corresponds to the mean field theory, which is known to be very inaccurate. The coexistence curve is of the form $y = x^{1/2}$ for Frumkin, while the exact lattice result is $y = x^{1/8}$ [15]. This has important consequences for the shape of the curves and for the sensitivity of the voltammogram to the interaction parameter of the adsorbate. In the case of the exact lattice gas isotherm the occupancy θ_{Cu} changes suddenly from an almost Langmuir type behaviour to a phase transition at the critical value of the

interaction parameter g_2 . In the mean field theory the change is much more gradual.

For the incommensurate case, or for the liquid mercury electrode, Frumkin's isotherm describes a gas-liquid transition, and not the solid-liquid transition [16]. This opens interesting possibilities about different types of transitions that are possible, and that we hope to discuss in the future. In the voltammogram the area under the spike is proportional to the charge transferred, not to the coverage of the surface, because the charge per adatom on the surface is not necessarily an entire number equal to the stoichiometric electrovalence [17].

In this paper we discuss further refinements and consequences of our model [1, 2]. We analyze the specific geometry predicted by it, we present a detailed discussion of the dependence of the model parameters on the potential bias, and we discuss briefly an extension to the dynamic case for slow voltage scanning rates. We use these results to explain recent experiments in which the concentration dependence was studied.

2 THE MODEL

The case of the UPD of Cu on Au(111) in the presence of H_2SO_4 has been extensively studied in recent times both experimentally [3, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27] and theoretically [28]. We should also mention that two recent studies of the kinetics of this system [29, 30] clearly indicate that in the shape of the voltammogram the first peak can be derived from equilibrium considerations, as was done in our earlier work, while in the second the kinetics is much slower and therefore observable from the analysis of the voltammogram.

In recent papers [1, 2] a model for the underpotential deposition of Cu on Au(111) in the presence of bisulfate ions was proposed. We summarize here the main results of our previous work.

In our model for the underpotential deposition of Cu on Au(111) in the presence of sulfuric acid, we assume that a well defined sequence of events takes place:

- Bisulfate ions are adsorbed at very positive potential, forming a $\sqrt{3} \times \sqrt{3}$ lattice on the gold surface. These bisulfate ions are desorbed as the potential is decreased, undergoing a hard hexagon like second order phase transition.
- Copper ions are then adsorbed on the free adsorption sites. The adsorption of copper produces a reabsorption of the bisulfate ions, which eventually will undergo the hard hexagon transition to rebuild the $\sqrt{3} \times \sqrt{3}$ lattice on the gold surface. This forms a honeycomb lattice for the adsorption of the remainder of the copper of the first peak.
- In the second peak the adsorbed bisulfate ions are displaced by copper ions from the $\sqrt{3} \times \sqrt{3}$ positions. However, they could still remain bound to the copper, which now forms a full monolayer on top of the Au(111) surface.

We assume that the bisulfate binds to the gold (111) surface in such a manner that the sulfur is directly on top of the adsorption site for the copper, three of the bisulfate oxygens being above and directly associated with the three gold atoms of the surface, which form a triangle about the adsorption site. Packing considerations indicate that two bisulfate groups cannot be adsorbed onto neighboring adsorption sites. The bisulfate ions will thus form a $\sqrt{3} \times \sqrt{3}$ film by occupying one of the three triangular sublattices Λ_T of the full triangular lattice of adsorption sites, with a maximum coverage of 1/3.

3 BISULFATE ADSORPTION

In our model it was assumed that the bisulfate ion formed a $\sqrt{3} \times \sqrt{3}$ template. This template leaves a honeycomb lattice of free sites for the adsorption of copper. The clear implication is that the first peak has 2/3 of a monolayer of Cu. The second peak corresponds to the replacement of the bisulfate by copper in the adlayer. We showed also that the broad foot of the first peak is due to a second order hard hexagon like transition, which is seen experimentally by Itaya[3] and Kolb [4]. We believe that the interpretation that the first peak corresponds to only 1/3 of a monolayer, based on the STM and LEED observations, is consistent with our model if it is the bisulfate ion that is seen.

In the present communication we amplify the previously proposed HB model [1, 2]. In this theory the broad foot of the first spike in the Cu-Au voltammogram is due a second order surface phase transition, similar to the hard hexagon phase transition [31]. This transition was actually observed by Itaya [3] and by Kolb [4].

In our theory in the initial stages of the process there is a strong coadsorption of copper with the bisulfate. At positive potentials ($V > 0.45$ volts with respect to the standard (Ag/AgCl) electrode), the bisulfate is strongly adsorbed onto the clean Au(111) surface. This means that there is an ordered $\sqrt{3} \times \sqrt{3}$ structure for these very positive potentials observable by STM or AFM. We assume that it retains its charge, and therefore, the bisulfate-bisulfate interaction is both long ranged and repulsive. The HSO_4^- sits in a tripod position, that is with its three oxygen atoms almost directly atop the Au atoms of the substrate, so that the adsorption of one HSO_4^- necessarily excludes nearest neighbor occupation. This makes the short ranged part of the surface interaction mathematically isomorphic to the hard hexagon problem, solved mathematically by Baxter[31]. There will be a second order, order-disorder phase transition when

$$\theta_S \geq \theta_c = 0.2764, \quad (1)$$

where θ_S is the fraction of the Au(111) lattice adsorption sites that are occupied by the bisulfate.

Consider a model in which there are three species, which for brevity we will call E (empty sites), Cu(copper) and S (bisulfate). In our lattice model of the surface there is no interaction between E and the other adsorbates, S strongly repels S, and S-Cu and Cu-Cu are strongly attractive. Models in which three components are adsorbed were recently discussed in the literature [32, 33, 34, 35].

We define [9, 10] the inner layer equivalent fugacity z_S for the adsorption of the bisulfate

$$z_S = \lambda_S(\psi)\rho_S^0(0, \psi) \quad (2)$$

where the sticking coefficient can be interpreted as $\lambda_S(\psi) = \exp[\beta\mu_S]$, with μ_S as the free energy change that occurs when a bisulfate ion binds to the gold surface, removing in the

process the adsorbed water. $\rho_S^0(0, \psi)$ is the inner layer local density of bisulfate for a local potential ψ .

We assume the simple exponential form [36] for the fugacity

$$z_S = \lambda_S^0 \rho_S^0(0, 0) e^{-\zeta_S \beta e(\psi - \psi_S^{Re})} \quad (3)$$

where $\beta = 1/kT$ is the Boltzmann thermal factor, the electrosorption valency of the bisulfate is $\zeta_S = -1$, and ψ_S^{Re} is the electrosorption reference potential, that depends on the nature of the substrate.

The adsorption isotherm for the hard hexagon model has been derived by Joyce [37]. His results can be fitted to Padé approximants [2]. For the high density, ordered phase

$$\theta_S^{high} = \frac{0.2764 + 0.155(z_S - 11.09) + 0.01(z_S - 11.09)^2}{1 + 0.5(z_S - 11.09) + 0.03(z_S - 11.09)^2} \quad z_S > 11.09. \quad (4)$$

For the low density, disordered phase,

$$\theta_S^{low} = \frac{0.709z_S + 0.0079z_S^2 + 0.0011z_S^3}{1 + 3.3z_S} \quad 0 < z_S < 11.09. \quad (5)$$

Consider now the adsorption of bisulfate onto Au(111) in the absence of copper. Using Eq.(3) with the effective charge of the adsorbed bisulfate $\zeta_S = -1$,

$$z_S = \lambda_S^0 \rho_S^0(0, 0) e^{\beta e(\psi - \psi_S^{Au})} = z_S^0 e^{\beta e(\psi - \psi_S^{Au})} \quad (6)$$

where we take

$$\psi_S^{Au} = 0.388V \quad (7)$$

and the bisulfate fugacity z_S is ($z_S^0 = 1$, $T = 298.16K$)

$$z_S = e^{38.922[\psi - \psi_S^{Au}]}, \quad (8)$$

The bisulfate is desorbed as the potential turns less positive. With these parameters the S lattice becomes disordered at about 0.45 V, which is when the copper starts to deposit. As long as the S template is disordered, the Cu is adsorbed randomly (probably next to the bisulfate).

The copper will start depositing at around $\psi = 0.4V$, but since the bisulfate is in its disordered phase, there should be no cooperative effects due to the copper-copper attraction on

the surface, and therefore, to a first approximation we may assume that the electrodeposition of copper follows a Langmuir-like (or Frumkin-Langmuir [36]) adsorption isotherm

$$\theta_{Cu} = \frac{\hat{z}_{Cu}}{1 + \hat{z}_{Cu}} \quad \theta_S < \theta_S^{crit} = 0.2764 \quad (9)$$

where ψ_{Cu}^{Au} is the electrodeposition reference potential of Cu on gold (111), and ζ_{Cu} is the effective electrovalence (certainly related to the electrosorption valency) of Cu (see the discussion below, Eq.(27)).

The electrosorption of bisulfate on polycrystalline copper [38, 39] shows that it binds much more strongly than to gold. We may assume that the electrosorption potential of the bisulfate varies linearly with the amount of copper in the surface. Thus, guided by the work of Trasatti on the influence of the anion on the potential of zero charge [40], we take

$$\psi_S^{Cu} < \psi_S^{Au}. \quad (10)$$

In our model, then

$$z_S = z_S^0 e^{-\zeta_S \beta e(\psi - \psi_S)}, \quad (11)$$

with

$$\psi_S = \psi_S^{Cu} \theta_{Cu} + (1 - \theta_{Cu}) \psi_S^{Au}, \quad (12)$$

In the presence of copper the bisulfate is then readsorbed. Eventually, the fraction of occupied sites will again surpass the critical value of 0.2764 (which corresponds to 83% of the occupancy of the template $\sqrt{3} \times \sqrt{3}$ lattice), and then there will be a first order transition for the copper on the honeycomb lattice of the Cu sites.[41] If we assume that the occupancy of copper $\theta_{Cu} = 1/3$ at the transition, we get that $\psi_S^{Cu} = -.302V$, which is in qualitative agreement with Wieckowski. [38, 39] In figure 1 we show the adsorption isotherm of the bisulfate as a function of potential [2].

4 THE FUGACITY OF COPPER

We recall that in the using the sticky site model [9, 10], there are two basic parameters that determine the phase behaviour of the adsorbed layer:

- The local fugacity $\hat{z} = \hat{z}_{Cu}$ of the two dimensional adsorbate gas is the product of the sticking probability λ_{Cu} and the contact density $\rho_{Cu}^0(0, \psi)$ of the ion i ,

$$\hat{z}_{Cu} = \lambda_{Cu} \rho_{Cu}^0(0, \psi) \quad (13)$$

- The lateral interaction parameter g_2

$$g_2 = g_2^0(\mathbf{R}_i, \mathbf{R}_j) \quad [i, j = \text{nearest lattice neighbors}], \quad (14)$$

where $\mathbf{R}_i, \mathbf{R}_j$ are the positions of the neighboring lattice sites i, j , and $g_2^0(r)$ is the pair correlation function in the electrode plane, but in the absence of the adsorption sites.

Both of these parameters depend on the applied potential ψ . Consider first the fugacity: The sticking probability is a function the bonding free energy ε_{Cu} of the adsorbate to the binding site. This quantity is independent of the ionic strength of the electrolyte, for a given potential. However, it will depend on the potential bias [36] at the surface. We write

$$\lambda_{Cu} = \lambda_{Cu}^0 e^{\beta \varepsilon_{Cu}}, \quad (15)$$

where the binding energy of the Cu ion depends on the potential bias of the metal substrate, or electrode,

$$\varepsilon_{Cu} = \zeta_{Cu} e[\psi - \psi_{Cu}^{Re}], \quad (16)$$

where e is the elementary charge, ψ is the potential at the electrode surface, and ψ_{Cu}^{Re} is the electrosorption reference potential. ζ_{Cu} is the effective charge of the adsorbed species at the surface, not necessarily equal to the electrovalence in solution.

The contact density $\rho_{Cu}^0(0, \psi)$ is also function of the potential bias. As a first approximation we will assume that the contact density is given by

$$\rho_{Cu}^0(0, \psi) = \rho_{Cu}^0(0, 0) e^{-\beta e \nu_{Cu} \psi} \quad (17)$$

where $\rho_{Cu}^0(0, 0)$ is the contact density at zero potential ψ , which for the Gouy-Chapman theory is equal to the bulk density ρ_{Cu} , and $e \nu_{Cu}$ is the full charge of the Cu ion. Therefore

$$\hat{z}_{Cu} = \lambda_{Cu}^0 \rho_{Cu}^0(0, 0) e^{\beta e [(\zeta_{Cu} - \nu_{Cu}) \psi - \zeta_{Cu} \psi_{Cu}^{Re}]} \quad (18)$$

Similarly, we write for the lateral interaction parameter g_2

$$g_2 = e^{-\beta\omega_2}. \quad (19)$$

where ω_2 is the potential of mean force between moieties adsorbed in neighboring sites. Since we know that the charges of these moieties change with ψ [42], ω_2 must also be a function of the potential bias ψ . (A detailed theory of a model which calculates this effect will be presented separately.)

Therefore we may expand about ψ_{Cu}^{Re}

$$\omega_2 = \omega_2^0 + e\alpha[\psi - \psi_{Cu}^{Re}] + \dots \quad (20)$$

where

$$\alpha = \frac{1}{e} \left| \frac{\partial \omega_2}{\partial \psi} \right|_{\psi=\psi_{Cu}^{Re}} \quad (21)$$

As was discussed in earlier work [9, 10], the coexistence curve is given by the exact condition

$$\hat{u} = \hat{z}[g_2]^{q_L/2} = 1, \quad (22)$$

where q_L is the number of neighbors of the lattice, 6 for the triangular (center filled regular hexagons) lattice and 3 for the honeycomb (empty center hexagons). If the parameter \hat{u} is less than unity then we are in the 1 phase region. If it is larger than 1, then we are in the two phase region. The coexistence curve is obtained setting $\hat{u} = 1$ in Eq.(22). For the triangular lattice [43]

$$\theta_T = (1/2) \left(1 \pm \left(1 - \frac{16g_2}{(g_2 - 1)^3(g_2 + 3)} \right)^{\frac{1}{3}} \right), \quad (23)$$

with a critical value $g_2^T = 3$. For the honeycomb lattice [41]

$$\theta_H = (1/2) \left(1 \pm \left(1 - \frac{16g_2^{3/2}(1 + g_2^{3/2})}{(g_2^{1/2} - 1)^3(g_2 - 1)^3} \right)^{\frac{1}{3}} \right), \quad (24)$$

with a critical value $g_2^H = (2 + \sqrt{3})^2 \simeq 13.93$.

As it was shown in earlier work, [10] the adsorption isotherm can be expressed as a generalized Langmuir adsorption isotherm of the form

$$\theta_{Cu} = \frac{\mathcal{A}(\hat{z}, \hat{u})}{1 + \mathcal{A}(\hat{z}, \hat{u})}, \quad (25)$$

where $\mathcal{A}(\hat{z}, \hat{u}) = \mathcal{A}$ is a polynomial in \hat{z} and \hat{u} . For the case in which there is a phase transition, θ_{Cu} is practically a step function which was represented by an error function in our previous work. A very simple and useful alternative form is

$$\mathcal{A} = \hat{z} + (g_2 - 1)\hat{u}^n, \quad (26)$$

where n is some entire number. The width of the transition spike is inversely proportional to n (actually to $n/4$), and will play the same role as the width parameter of our previous work[44]. It is related to instrumental width, substrate domain size and defects on the surface.

Combining Eq.(18)- Eq.(20) and Eq.(22), we get that at the transition point, ψ_T

$$\hat{u}_{Cu} = \lambda_{Cu}^0 \rho_{Cu}^0(0, 0) e^{\beta e[(\zeta_{Cu} - \nu_{Cu} - q_L \alpha/2)\psi_T - (\zeta_{Cu} - q_L \alpha/2)\psi_{Cu}^{Re} - q_L \omega_2^0/2e]} = 1. \quad (27)$$

The relation of the parameters in this formula to the electron transfer coefficients will be discussed in future work.

5 KINETIC MODEL

There is a very extensive literature on the voltammograms for the electrodeposition of metals, starting with the early work of Koryta [45], Delahay [46] Brdicka [47], Guidelli[48], Laviron [49], Lorenz[50], Reinmuth[51], Sadkowski[52] and Lantelme[54]. However these models do not correspond to the case of adsorption onto a lattice with cooperative effects. In our general statistical mechanics treatment of phase transitions in the ad-layers [10] the adsorption isotherm is written in the form of a Padé approximant, which represents to any required precision the exact coexistence line and universal critical behaviour. This form of

the isotherm lends itself to a simple way to include kinetic effects, which in the limit of very slow scanning rates gives back the required equilibrium phase behaviour.

A kinetic equation for the fraction of occupied sites θ_{Cu} of the honeycomb or triangular sublattices of the original lattice can be obtained for a simple probabilistic model, in which the probability of a site to be occupied by Cu is proportional to the density of Cu at the electrode surface and the number of free sites.

$$\rho_{Cu}(0, \psi)(1 - \theta_{Cu})$$

The probability of an ion that is adsorbed to be dissolved is proportional to θ_{Cu} . Therefore, the rate of change is

$$\frac{\partial \theta_{Cu}}{\partial t} = K_a \rho_{Cu}(0, \psi)(1 - \theta_{Cu}) - K_d \theta_{Cu} \quad (28)$$

The two reaction rate constants K_a and K_d must satisfy at equilibrium the relation Eq.(25) and therefore

$$\frac{K_a \rho_{Cu}(0, \psi)}{K_d} = A(\hat{u}) \quad (29)$$

There are many ways in which this relation can be satisfied: If K_d is of the exponential form [36]

$$K_d = K_0 e^{\alpha T \psi}, \quad (30)$$

then

$$K_a \rho_{Cu}(0, \psi) = K_0 e^{\alpha T \psi} A(\hat{u}), \quad (31)$$

We write Eq.(28) in the form

$$\frac{\partial \theta_{Cu}}{\partial t} = -\theta_{Cu} K_{ad} + K_a \rho_{Cu}(0, \psi), \quad (32)$$

where

$$K_{ad} = K_a \rho_{Cu}(0, \psi) + K_d. \quad (33)$$

This is our nonlinear kinetic equation, which together with the diffusion equation constitutes a system of equations that can be solved numerically. Interesting asymptotic solutions for limiting cases can be obtained, that will be discussed in a separate paper.

If we neglect diffusion then an asymptotic solution for slow scanning rates can be obtained.

We consider here the case in which ψ is the electrode potential and

$$\psi = \psi_{in} + vt \quad (34)$$

where ψ_{in} is the initial value of the potential, and v is the scanning rate.

The solution of Eq(32) is [55]:

$$\theta_{Cu}(t) = \theta_{Cu}^{\infty}(t) + [\theta_{Cu}(0) - \theta_{Cu}^{\infty}(0)] e^{-\int_0^t dt_1 \{K_{ad}(t_1)\}} - \int_0^t dt_1 \frac{\partial \theta_{Cu}^{\infty}(t_1)}{\partial t_1} e^{-\int_{t_1}^t dt_2 \{K_{ad}(t_2)\}}, \quad (35)$$

where

$$\theta_{Cu}^{\infty}(t) = \frac{K_a(t)\rho_{Cu}(0,t)}{K_{ad}(t)} = \frac{\mathcal{A}(\hat{u}_{Cu}(t))}{1 + \mathcal{A}(\hat{u}_{Cu}(t))}, \quad (36)$$

is the equilibrium fraction of occupied sites for the potential at time t . Changing now variables to ψ , and integrating by parts we get the expansion in terms of v :

$$\theta_{Cu}(\psi) = \theta_{Cu}^{\infty}(\psi) - \frac{v}{K_{ad}(\psi)} \frac{\partial \theta_{Cu}^{\infty}(\psi)}{\partial \psi} + \frac{v^2}{K_{ad}(\psi)} \frac{\partial}{\partial \psi} \left[\frac{1}{K_{ad}(\psi)} \frac{\partial \theta_{Cu}^{\infty}(\psi)}{\partial \psi} \right] - \dots \quad (37)$$

This equation should be useful in calculating the overall kinetic constants K_{ad} from the shifts in the voltammogram.

A simple useful formula that can be obtained from this equation is that for small scanning rates v the zero scanning rate limit is given by

$$\theta_{Cu}^{\infty}(\psi) = (1/2) [\theta_{Cu}^{oxid}(\psi) + \theta_{Cu}^{red}(\psi)], \quad (38)$$

where $\theta_{Cu}^{oxid}(\psi)$ is the isotherm for oxidation scan and $\theta_{Cu}^{red}(\psi)$ for the reduction scan.

6 THE CURRENT IN THE VOLTAMMOGRAM

Consider the electrode interface, in which a current flows. We have specifically in mind the case of the UPD of Cu onto Au(111). In this case there are two ions that participate in the transport of charge:

- The bisulfate, that carries a negative charge which it keeps when adsorbed onto the surface. Therefore, it will contribute only to the capacitive current density j_C . The other contribution to j_C is from the diffuse layer.
- The copper, which is adsorbed and discharged to some extent. It's electrovalence will change from ν_{Cu} in the bulk phase to ζ_{Cu} at the electrode interface. Furthermore, ζ_{Cu} should be a function of the potential ψ .

Therefore, the total current density is (for a recent discussion see, for example the work of De Levie [53] and Lantelme [54])

$$j_T = j_C + j_F \quad (39)$$

where j_T is the total current density, j_C is the capacitive contribution and j_F is the Faradaic contribution. If we neglect double layer effects, then the capacitive current is due to the bisulfate, and the faradaic current almost exclusively to the discharge of the copper ions.

Then

$$j_C = (1/A) \left[C_i + \psi \frac{dC_i}{d\psi} \right] \frac{d\psi}{dt} \quad (40)$$

gives the current due to the discharge of the capacitor as well as its change in integral capacitance C_i . A is the area of the electrode.

The current associated with the cation (in this case the copper) can be written as

$$j_F = (M/A)e \left[-\theta_{Cu} \frac{d\zeta_{Cu}}{d\psi} + (\nu_{Cu} - \zeta_{Cu}) \frac{d\theta_{Cu}}{d\psi} \right] \frac{d\psi}{dt} \quad (41)$$

where M is the number of adsorption sites per area A , e is the elementary charge, ζ_{Cu} is the actual charge of the adsorbed copper and ψ the potential.

In accordance with the quantum theory [42], the charge of the adsorbate will change with the applied potential because the electron density at the surface is changing. Intuitively we take the exponential form

$$\zeta_1(t) = e^{\omega_\zeta(\psi - \psi_1^{Re})}, \quad (42)$$

where ω_ζ and ψ_1^{Re} are adjustable parameters.

In figure 2 we show a comparison of the current density obtained from the copper contribution of our model to the oxidation branch of Kolb's voltammogram. We have adjusted the position of the hard hexagon transition to .22V, the position of the first peak to .21V.

7 GEOMETRY OF THE MODEL

We discuss now some geometrical properties of our model. We recall that we assume that the bisulfate ion formed a $\sqrt{3} \times \sqrt{3}$ template. This template leaves a honeycomb lattice of free sites for the adsorption of copper. The clear implication is that the first peak has 2/3 of a monolayer of Cu. In this section we want to show that the bisulfate actually protrudes from the surface, and therefore the 1/3 of a monolayer seen by the STM and LEED observations is consistent with our model.

The vertical distance between the substrate Au(111) plane and the adsorbed copper can be estimated to be 2.22 Å , by taking the mean distance in metallic gold and in metallic copper. From early EXAFS experiments [18, 19, 20] and recent theory [28] we know that the gold (or copper) distance to the oxygens in the bisulfate is between 1.95Å and 2.1 Å , so that from the dimensions of the bisulfate ions, it should be between 1.84Å and, if we count the hydrogen of the bisulfate, 2.13Å higher than the plane where the copper lies. Assuming the same geometry on a clean Au(111) surface the bisulfate layer should stand about 4.06-4.35 Å above the Au surface. However, the STM cannot measure absolute heights, and therefore, both cases appear as a $\sqrt{3} \times \sqrt{3}$ overlayer.

An observation to be made is that the Cu – O distances appear at 1.81 Å if we assume an undistorted bisulfate ion and copper honeycomb lattice. This is a bit lower than the expected value of 1.95Å . Therefore we would expect that the adsorbed ion be deformed so that the oxygens lie about .2 Å below the line of the copper atoms, which would relieve the stress, but at the same time create a activation energy barrier for the desorption of the copper. This again is consistent with the experimental observations.

The proposed coordinates are shown in Table 1, and the geometry in figure 3.

8 CONCENTRATION DEPENDENCE

If all the parameters stay the same as the concentration of copper is changed, a shift in the concentration will necessarily imply a shift in the transition potential

$$\Delta\psi_T^{Re} = \frac{kT}{e(\nu_{Cu} + q_L\alpha/2 - \zeta_{Cu})} \Delta \ln[\rho_{Cu}(0, 0)]. \quad (43)$$

For a tenfold increase in concentration the potential shift is

$$\Delta\psi_T = \frac{59.2mV}{\nu_{eff}}, \quad (44)$$

where ν_{eff} is the effective charge obtained directly from the equation Eq.(27)

$$\nu_{eff} = \nu_{Cu} + q_L\alpha/2 - \zeta_{Cu}. \quad (45)$$

We are now in position to discuss the recent experiments of Omar et al. [30] and Höltzle et al [29]. Using the results of the local kinetic theory [55] we can estimate the positions of the peaks in the experiment of Omar et al. We notice that the relative shift of the bulk deposition edge corresponds exactly to the electrovalence of copper, 2. We should remark that this is a bit surprising, since one would expect that it should scale to the activity of the copper, not its concentration. However this also means that the contact density $\rho_{Cu}(0, \psi)$ in our model scales almost exactly to the Gouy-Chapman estimate Eq.(17), which is non-trivial and reassuring. We recall that our interface is not planar, our solution is molecular, and the position at which $\rho_{Cu}(0, \psi)$ is taken is some average over the positions in the metal electrolyte interface. We know that the contact theorems are satisfied by these averages, and this is probably the reason why the Gouy-Chapman estimate is so accurate.

If we use the shifts of the edge to compute the effective charge Eq.(45) for the peaks in the voltammogram we find that the effective charge for the second peak is 20 % higher than 2, and that for the first peak we get about 1, which is very difficult to explain in terms of individual fugacities or the Nernst equation [30].

The inclusion of the variation of the pair correlation functions between adsorbed particles with ψ removes these difficulties. The results of table 2 show that the remarkable accuracy of the Gouy-Chapman estimate holds also for other transition points. However the actual values of the charges cannot be reconciled with the other experimental evidence.

For the second peak a charge bigger than two cannot be explained in any other way but by including the variation of g_2 with potential ψ . The value $\alpha = 0.14$ seems reasonable.

The apparent charge for the first peak $\nu_{eff} = 1$ is definitely inconsistent with the experimental evidence and in particular with the integrated charge shown in fig.6 by the same authors, where the ratio of the charges of both peaks is very closely 1, so that each peak corresponds to 50% of the monolayer charge. If we assume only 1/3 coverage by copper as has been indicated in the literature [3, 4], the charge would be only 16% of the monolayer, clearly impossible. The explanation that the remainder of the charge is due to desorption of the sulfate is inconsistent with the EXAFS experiment [18], with the radiotracer experiment[38], and with the microbalance experiment[26], all of which indicate that there is strong bisulfate adsorption even after the full monolayer is deposited.

The situation improves if we take the 2/3 monolayer coverage predicted by the HB model [1, 2]. We get 50 % of the monolayer for each peak's charge when $\nu_{Cu} - \zeta_{Cu} = 1.0$ and $\zeta_{Cu} = 1.0$. The value $\zeta_{Cu} = 0.5$, which implies $\nu_{eff} - \zeta_{Cu} = 1.5$ satisfies the 60% for the first peak charge requirement of Kolb's voltammogramm, and produces a neutral film near the expected value of the point of zero charge for this system. We believe that this last one is a more plausible value of the charge, since charge neutrality explains the lifting of the reconstruction of the gold surface by the adsorbed copper layer.

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Table 1

STRUCTURE OF THE OVERLAYER

	undistorted-stressed			distorted-relaxed		
	x	y	z	x	y	z
Au1	0	-1.66	0			
Au2,3	± 1.44	0.88	0			
Cu1,2	± 2.88	0	2.22			
Cu3,4,5,6	± 1.44	± 2.49	2.22			
O1	0	-1.39	2.09	0	-1.32	1.9
O2,3	± 1.21	0.70	2.09	± 1.15	0.66	1.9
O4	0	0	4.065			
S	0	0	2.58			
H	0	0.90	4.35			

Caption Table 1

Structure of the adlayer with 1/3 coverage of bisulfate and 2/3 of Cu. The stressed structure was made using an undistorted bisulfate ion. In the relaxed structure the bisulfate ion was squeezed so that the O - O distance is shortened from 2.42 Å to 2.30 Å , while the copper-oxygen goes from 1.81 to 1.87 Å.

Table 2
SHIFTS OF THE VOLTAMMOGRAM'S PEAKS

	Exp.(mV)			Shifts(mV)		e		
	#1	#2	#3	#2→#1	#3→#2	Eff.Chg.	Real.Chg.	α
Edge	299	270	241	29	29	2.04	0	
Foot	557	500	458	57	42(?)	-		
1st. peak	554	496	444	58	52	1.02/1.14	0.5	-0.33/-0.25
2st. peak	352	327	303	25	24	2.37/2.47	0	0.14

Caption Table 2

Shifts of the voltammogram's peaks with concentration from Omar et al [30], Figure 4.

Experiment # 1: $9.10^{-2} H_2SO_4$, $5.10^{-2} CuSO_4$

Experiment # 2: $9.10^{-2} H_2SO_4$, $5.10^{-3} CuSO_4$

Experiment # 3 : $9.10^{-2} H_2SO_4$, $5.10^{-4} CuSO_4$

The effective charge is evaluated using Eq.(45). α is evaluated using $\zeta_{Cu} = 0.5$ for the first peak, and $\zeta_{Cu} = 0$ for the second peak.

The foot corresponds to the hard hexagon transition, which we cannot estimate accurately from the graphs.

FIGURE CAPTIONS

FIGURE 1

Fraction of sites occupied by HSO_4^- . Dotted line represents the clean gold surface. Solid line the case with copper coadsorption. This graph is qualitative [2].

FIGURE 2

Comparison of the theory to the oxidation branch of Kolb's voltammogram [21], for $0.1N H_2SO_4$, $10^{-3}N CuSO_4$ and a scanning rate of $1mV/s$. The theory includes only the copper contribution.

FIGURE 3

Geometry of the adlayer with $1/3$ bisulfate and $2/3$ of copper. The copper ring holds the bisulfate structure, but the top of the bisulfate is still higher than the copper.

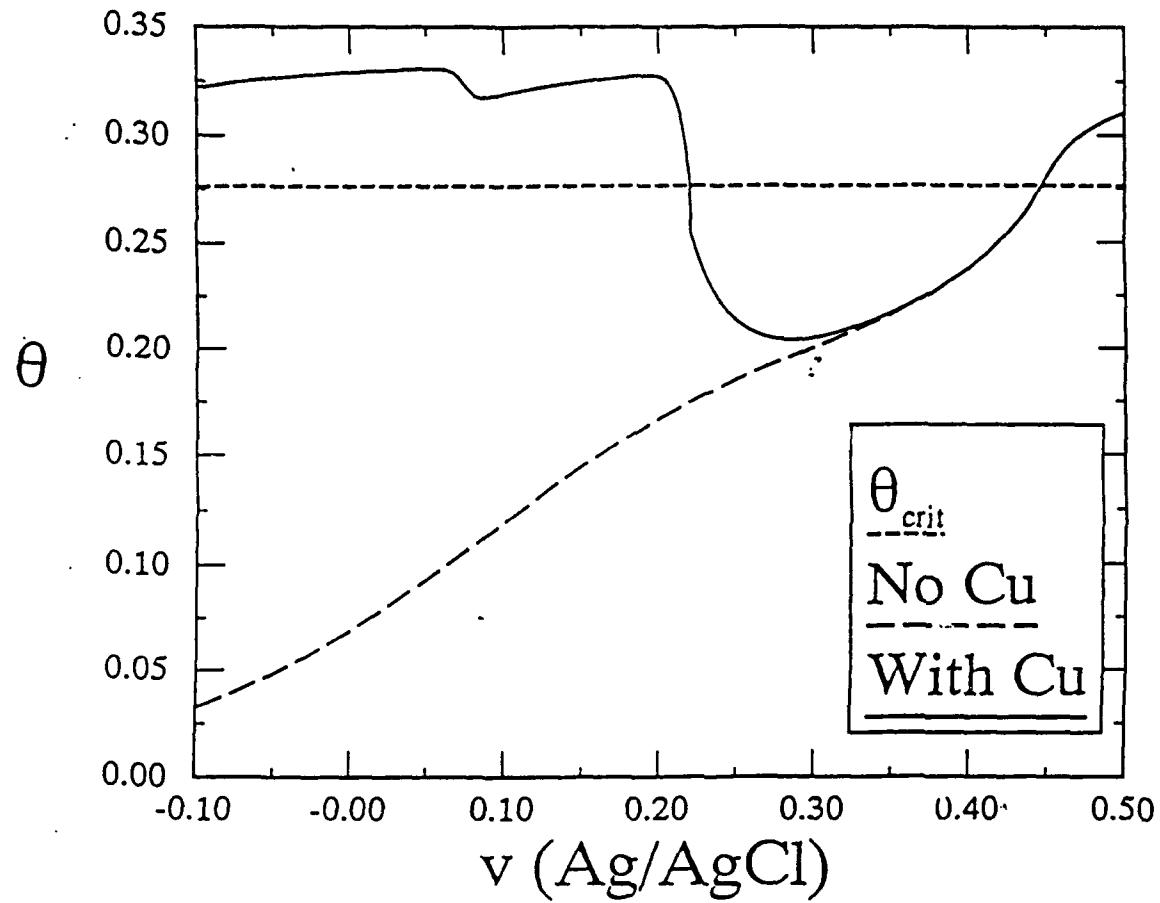


Figure 1: Fraction of occupied sites by HSO_4^- . Dotted line represents the case of a clean gold (111) surface. Solid line corresponds to our model of copper coadsorption.

Figure 2

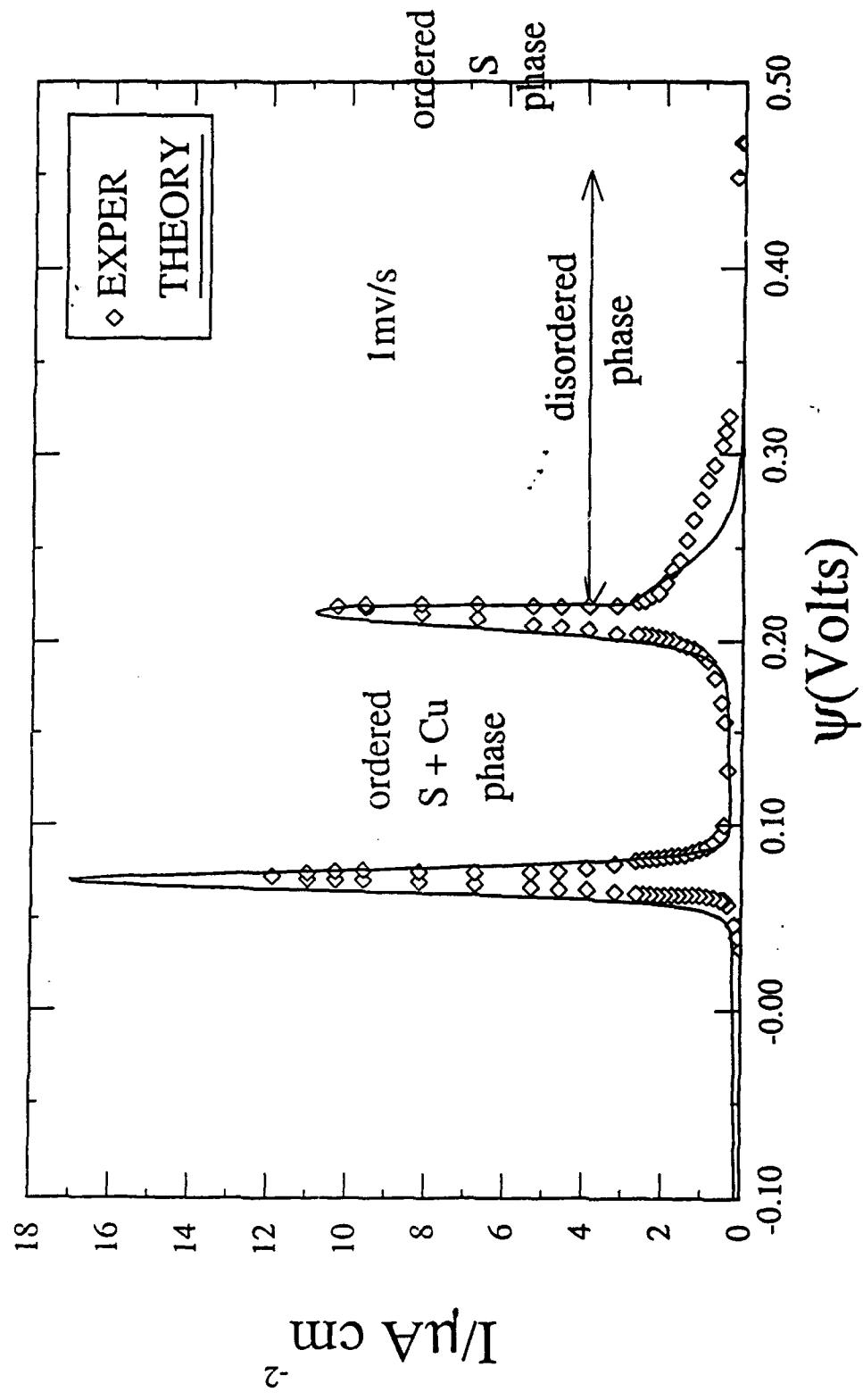


FIGURE 3

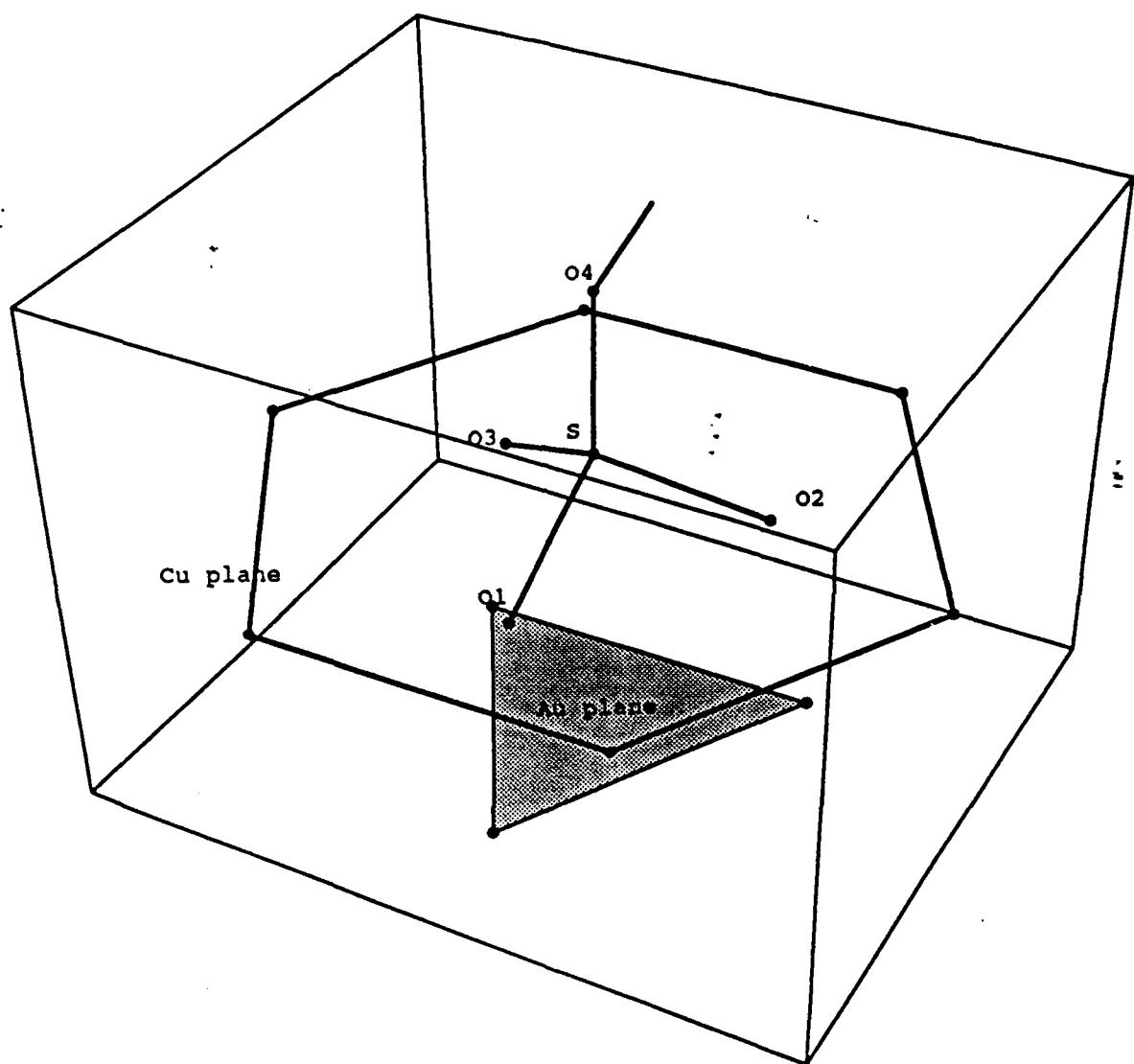


Figure 6

